

Research experience and plans

1 Background

In modern electronic structure calculations, the goal is to solve the Schrödinger equation, $\hat{H}\Psi = E\Psi$, for the N -electron system of interest, where E is the total energy of the system and Ψ the $3N$ -dimensional wavefunction. This is a formidable computational task, and for systems with more than 10 electrons, solutions of high accuracy are extremely hard to obtain with ab initio methods. The major problem has been the slow convergence of the N -particle basis set expansions of the $3N$ -dimensional wavefunction. In density functional theory (DFT) [1], one tries to avoid this problem by expressing the energy as a functional of the electron density. The idea is to map the difficult problem of interacting electrons in an external potential to the simpler one of noninteracting electrons moving in a local effective potential yielding the same density. The only unknown part of this functional is the exchange-correlation (XC) energy. Therefore, the central task of this approach has been to find accurate-enough XC functionals. Because DFT is a fast method capable of treating large systems and no other methods can achieve comparable accuracy at the same computational cost, development of DFT has provided alternative to conventional wavefunction methods. With the rapid advent of reliable density functionals, this theory has become the most popular method in electronic structure calculations of molecules and solids, and has made a notable impact on condensed matter physics [2], chemistry [3], and molecular biology [4].

The simplest construction of the XC functional $E_{xc}[n]$ is the local spin density approximation (LSDA) [1], which only uses local spin densities $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ to calculate the exchange-correlation energy. While LSDA has been successful in condensed matter physics, it tends to overbind molecules. One important step to go beyond LSD is the generalized gradient approximation (GGA) [5, 6], which employs not only the local densities but also their gradients $\nabla n_{\uparrow}(\mathbf{r})$ and $\nabla n_{\downarrow}(\mathbf{r})$. With the advent of GGA, DFT has been developed from being a qualitatively useful method to being a quantitatively popular tool in electronic structure calculations of molecules as well.

Since the commonly used GGAs show the limited accuracy to order of several kcal/mol for typical thermochemical data such as atomization energies, a systematic way to improve upon GGAs is to construct meta-GGA functionals [7] by making use of additional semilocal information such as the Kohn-Sham kinetic energy densities $\tau_{\sigma}(\mathbf{r})$, where $\sigma = \uparrow, \downarrow$. Several meta-GGAs [8, 9, 10, 11, 12] have been constructed with their improved accuracy to order of about 3 kcal/mol for atomization energies. This is not too far from “chemical accuracy” (atomization energy errors of order 1 kcal/mol = 0.0434 eV). However, these meta-GGA functionals contain at least one empirical parameter fixed by a fit to atomization energies. It may be risky to apply density functionals with the accuracy relying upon adjustment of empirical parameters to the classes of systems or problems outside their training sets. While the exact form of the universal functional remains unknown, many exact constraints on this functional have been discovered [13]. This makes it possible to construct nonempirical functionals without the need of any parameters fitted to experiment. Because of the satisfaction of many correct constraints, nonempirical functionals [5, 7] can be transferable and thus uniformly accurate for diverse systems. Uniform accuracy can effectively eliminate the need to use different functionals for different classes of problems, and the difficulties that arise when these classes combine (e.g., chemical reactions on catalyst surfaces or chemisorptions).

2 Completed work

I will briefly discuss my main work below. While the remaining work listed in my bibliography are not introduced here, but a reading of their titles will convey a general idea of them.

2.1 Nonempirical construction of a meta-GGA

The most elegant nonempirical construction of GGA might be the one designed by Perdew, Burke, and Ernzerhof (PBE) [5], based on the known properties of the XC energy. The PBE GGA satisfies as many correct conditions as a nonempirical GGA can. To improve the accuracy of GGA, a natural way is to construct a meta-GGA by imposing additional correct constraints, without losing those that GGA has already satisfied. This may be achieved by absorbing the kinetic energy density

$$\tau_{\sigma}(\mathbf{r}) = \sum_{k=1}^{\text{occup}} \frac{\hbar^2}{2m} |\nabla \psi_{k\sigma}(\mathbf{r})|^2, \quad (1)$$

where $\psi_{k\sigma}$ are the occupied Kohn-Sham orbitals, as an additional ingredient. The inclusion of the kinetic energy density as an additional local ingredient allows a meta-GGA to satisfy additional exact conditions. Thus meta-GGA should improve upon GGA if all the correct properties of GGA are preserved, while adding others. The kinetic energy density is usually accessible in every DFT calculation.

Starting with the PBE GGA, making use of the properties of the kinetic energy density, and following the philosophy of nonempiricism, Tao, Perdew, Staroverov, and Scuseria (TPSS) [7] have constructed a nonempirical meta-GGA,

$$E_{\text{xc}}^{\text{MGGGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \epsilon_{\text{xc}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}), \quad (2)$$

where $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$ is the total density and $\epsilon_{\text{xc}}(\mathbf{r})$ the exchange-correlation energy per electron. Extensive tests [7, 14, 15, 16, 17] on molecules, solids, and solid surfaces show that the TPSS meta-GGA generally improves upon previously constructed nonempirical functionals and approaches or exceeds best semiempirical functionals even for molecules. Our test [18] on rare-gas dimers shows that this functional provides a much more realistic description of the short-range part of the van der Waals (vdW) interaction than LSD, suggesting that TPSS can serve as a platform on which higher-level density functionals (see section 2.3) can be constructed.

2.2 Nonempirical current-density functionals constructed from conventional density functionals

Conventional density functional theory can now achieve useful accuracy in the order of a few kcal/mol in thermochemistry such as bond breaking, atomization, ionization, etc. Bond breaking and atomization involves free atoms in open-shell states. Electrons in such an atom can occupy different (degenerate) orbitals with the same total energy. Since these degenerate orbitals usually do not have the equivalent densities, the conventional DFT [19] methods as discussed above fail to reproduce the correct degeneracy. Atomic open-shell reference calculations are therefore problematic. Unfortunately, the discrepancy due to electrons occupying degenerate orbitals in different ways is sometimes more than 5 kcal/mol for GGAs [20, 21, 22, 23] and even larger (more than 10 kcal/mol) for meta-GGAs (e.g. in an oxygen atom) [21, 23]. A way to solve this problem is to introduce the (paramagnetic) orbital current density

$$\mathbf{j}_p(\mathbf{r}) = \frac{\hbar}{2mi} \sum_{k\sigma} [\psi_{k\sigma}^*(\mathbf{r}) \nabla \psi_{k\sigma}(\mathbf{r}) - \nabla \psi_{k\sigma}^*(\mathbf{r}) \psi_{k\sigma}(\mathbf{r})] \quad (3)$$

as another basic variable into the conventional DFT methods. Current-density functional theory [24, 25] methods can reduce these degeneracy problems and may properly describe systems in a magnetic field that produces true orbital currents. While several papers [21, 22, 26, 27, 28] in this direction were published, systematic construction of reliable current-density functionals is not available.

By examining gauge transformation of the usual local ingredients of the conventional density functionals, we have found [29] that current-density functionals may be constructed systematically from conventional ones by explicit inclusion of paramagnetic current density in the XC functionals of current-density functional theory.

When the current $\mathbf{j}_p(\mathbf{r})$ is present, Vignale and Rasolt [24, 25] have extended the Kohn-Sham theorems and proposed an additive correction valid to second order in the gauge-invariant vorticity $\boldsymbol{\nu} = \nabla \times (\mathbf{j}_p/n)$:

$$E_{xc}[n, \mathbf{j}_p] = E_{xc}[n, \mathbf{j}_p = 0] + \Delta E_{xc}^{\text{VR}}[n, \boldsymbol{\nu}]. \quad (4)$$

Apart from spin-polarization effects, their correction is unambiguous for a GGA. But for a meta-GGA, one needs to know how to go back from the orbital kinetic energy density $\tau([n, \mathbf{j}_p]; \mathbf{r})$ of Eq. (1) to $\tau([n, 0]; \mathbf{r})$ (for use in $E_{xc}[n, \mathbf{j}_p = 0]$); we have shown [23] how to do this. Numerical tests on the degeneracies for open-shell atoms show that current-density corrections dramatically reduce the error of GGA from 2 to 1 kcal/mol, and of meta-GGA from 5 to 2 kcal/mol. This achievement may significantly expand the scope of application for conventional density functionals.

2.3 Construction of self-interaction-free density functionals

Construction of self-interaction-free density functionals is substantial for electronic structure calculations of molecules and solids. Self-interaction correction [30] is needed to properly treat many physical and chemical problems such as the bandgap, cohesive energy, electronic charge transfer, energy barrier, excitation energy, etc. Numerical study [31] shows that self-interaction-free functionals can yield usefully accurate energy barrier height of a chemical reaction. This remarkable achievement makes it possible to investigate the dynamical processes of a chemical reaction.

For any one-electron system, because the electron can not interact with itself, $E_x[n] = -U[n]$, where $U[n]$ is the Hartree potential energy, and $E_c[n_\sigma, 0] = 0$. While the TPSS correlation is designed to be self-interaction-free (i.e., $E_c^{\text{MGGA}}[n_\sigma, 0] = 0$), the TPSS exchange is not, except for the ground-state hydrogen atom. Therefore, an important flaw remaining in the TPSS approximation is the self-interaction error in the exchange part. This problem may be solved by constructing a self-interaction-free hyper-GGA via introducing the exact-exchange energy per electron as an additional local ingredient beyond those of the meta-GGA.

A hyper-GGA (HGGA) exchange-correlation energy per electron may be written as

$$\epsilon_{xc}^{\text{HGGA}} = \epsilon_x^{\text{exact}}(\mathbf{r}) + a(\mathbf{r})[\epsilon_x^{\text{TPSS}}(\mathbf{r}) - \epsilon_x^{\text{exact}}(\mathbf{r})] + \epsilon_c^{\text{dyn}}(\mathbf{r}), \quad (5)$$

where $a(\mathbf{r})$ is the local exact-exchange mixing parameter which, like global hybrids, is constrained to be in the range of $0 \leq a \leq 1$, (in global hybrids, a is a position-independent constant), and $\epsilon_c^{\text{dyn}} = \epsilon_c^{\text{TPSS}}$ is the dynamical correlation. The second term is designed to account for the static correlation which is absent in TPSS and other non-hybrid functionals. The main task here is to construct the exact-exchange mixing parameter $a(\mathbf{r})$ by imposing additional constraints without losing those that TPSS has already satisfied.

Recently, Perdew, Staroverov, Tao, and Scuseria (PSTS) [32] have constructed a hyper-GGA, which satisfies almost all the exact constraints possible for a hyper-GGA. This hyper-GGA retains the advantage of error cancellation between semilocal exchange and semilocal correlation. Preliminary tests show that the PSTS hyper-GGA yields accurate atomization energies and significantly improves the energy barriers upon semilocal functionals.

2.4 The role of quantum stress in descriptive chemistry

Atomic shell structure, electron pair bonds, lone electron pairs, π -electron subsystems, etc., are some of the most important concepts in descriptive chemistry and play a significant role in modern electronic structure theory. These concepts help us to visualize the bonding between atoms and the geometry of a molecule in terms of small groups of localized electrons (e.g. two electrons of opposite spin in a simple covalent bond) and therefore play an important role in determining new molecular structures and in describing structural changes due to chemical reactions. A precise quantitative description of these small groups of localized electrons has been sought for a long time [33, 34], but none of the solutions proposed so far is completely satisfactory.

Recently, we have proposed a physical way of looking at atomic shells and bonds based on the idea of *quantum stress focusing*, by which we mean the spontaneous formation of surfaces on which the electronic pressure attains an extremum. We show [35] that a physically motivated electron localization function (ELF) can be constructed from the electronic pressure, which can be calculated from DFT. Application to atoms shows that the new ELF gives an excellent visualization of atomic shell structure.

2.5 Time-dependent density functional theory

The static DFT is a mainstream electronic structure theory of many-electron systems, which has achieved a high-level sophistication. While a ladder of highly accurate XC functionals have been constructed, they are essentially not suitable for the description of time-dependent processes and excited states, because these density functionals are only protected by the ground-state Hohenberg-Kohn [36] variational principle. This limitation has been overcome by the most important extension of DFT—time-dependent DFT (TDDFT) [37, 38]. In recent years TDDFT has rapidly grown into a popular method for the investigation of dynamical properties of many-electron systems [39]. It follows the Kohn-Sham strategy and maps the complicated problem of interacting electrons in a time-dependent external potential $v(\mathbf{r}, t)$ to a simpler one of noninteracting electrons moving in a self-consistent time-dependent effective potential $v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + u_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t)$, which generates the density $n(\mathbf{r}, t)$ of the interacting system. Here $u_H(\mathbf{r}, t)$ is the Hartree potential given by $u_H(\mathbf{r}, t) = \int d^3r' n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'|$, and $v_{xc}(\mathbf{r}, t)$ is the dynamical XC potential defined by $v_{xc}(\mathbf{r}, t) \equiv \delta A_{xc}[n]/\delta n(\mathbf{r}, t)$, with $A_{xc}[n]$ being the time-dependent XC functional or XC action, the analogue of the static functional $E_{xc}[n_0]$. In principle, This is an exact many-body theory. In practice, the dynamical XC potential has to be approximated.

The simplest construction of the dynamical XC potential is the adiabatic approximation [40] which employs the same form of the static XC potential, but replaces the equilibrium density $n_0(\mathbf{r})$ with the instantaneous density $n(\mathbf{r}, t)$. While the adiabatic approximation works well for single-particle excitations of atoms and molecules, it fails for multi-particle excitations or charge transfer, and gives no dissipation. Furthermore, it severely overestimates the dielectric polarizability of insulators, in spite of the fact that this is a “zero-frequency property”. Early attempts [41] to correct the adiabatic approximation without leaving the framework of the local density approximation were found [42, 43] to violate the “harmonic potential theorem”. Vignale and Kohn (VK) [44, 45] pointed out that a dynamical

cal local density approximation is still permissible if one switches the basic variable from the density to the current density $\mathbf{j}(\mathbf{r}, t)$. Starting from this observation, they developed the time-dependent current density functional theory in the linear response regime. However the VK theory relies on a *double local density approximation* (double LDA), namely, both the ground-state density and the external potential are assumed to be slowly varying in space.

We have presented a method [46] to avoid one of the two local density approximations on which the VK theory is based, namely the approximation that the ground-state density is slowly varying. The basic idea is to describe the time evolution of the system in a non-inertial reference frame – the Lagrangian frame or L-frame – in which the particle density is time-independent and the macroscopic current vanishes [47]. The advantage of working in this reference frame is that the extreme nonlocality that plagues the time-dependent XC functional in the laboratory frame is cured. So, while the Hamiltonian in the L-frame is still time-dependent and inhomogeneous, the fact that the particles in this reference frame cannot move in or out of a given volume element enables us to apply the powerful technology of the GGA [5] and meta-GGA [7] to the calculation of the XC stress tensor. The XC field can be calculated from the expression [46]

$$-eE_{xc,\mu}(\mathbf{r}, \omega) = \partial_\mu V_{xc}^{\text{ad}}(\mathbf{r}, \omega) + \frac{1}{n_0} \partial_\nu \Delta P_{\mu\nu}^{\text{xc}}(\mathbf{r}, \omega), \quad (6)$$

where V_{xc}^{ad} is the adiabatic approximation and $\Delta P_{\mu\nu}^{\text{xc}}$ is the dynamical stress tensor whose divergence yields the linear-order correction to the adiabatic approximation. The two conditions for the validity of this treatment are (i) the deformation of the ground-state density must be small and (ii) it must be slowly varying in space, so that its spatial derivative can be neglected. These conditions are more easily met than the condition of slowly varying density. Therefore our dynamical XC potential should be valid in a wider class of systems than the VK potential, while reducing to the latter in the limit in which the equilibrium density is slowly varying.

3 Research plans

3.1 Refinement of the meta-GGA and hybrid functionals

Accurate description of bandgap, cohesive energy, electronic charge transfer, energy barrier, excitation energy, etc. is significantly important in the design, synthesis, and improvement of new materials. Although semilocal functionals tend to underestimate these properties. hybrid functionals with proper amount of exact exchange can effectively reduce the difficulty.

While the TPSS meta-GGA correlation has a quite restricted form that was designed to satisfy as many constraints as a meta-GGA can, there is some flexibility in the construction of TPSS exchange. We may improve the performance of the TPSS meta-GGA and its hybrid by refining its exchange part. I have constructed a nonempirical meta-GGA exchange functional from the density matrix expansion. Preliminary tests show that, when combined with TPSS correlation, it yields very accurate bond lengths and atomization energies. The following work is to give this new functional a comprehensive assesment.

3.2 Current-density functional Theory

Current-density functionals may be constructed [23] from conventional ones, as discussed in section 2.2. The key ingredient of the current-density functionals is the diamagnetic (Landau) susceptibility χ_L which can be calculated [48] within the random phase approximation (RPA). Numerical tests on

open-shell atoms show that the Vignale-Rasolt correction of Eq. (4) is in the right direction, but is only about half of what is needed. This may be due to use of the RPA χ_L away from the high-density limit, or to the assumed exchange-like scaling when the Vignale-Rasolt correction of Eq. (4) is generalized to spin-polarized systems, or both.

Recently we [49] have calculated the diamagnetic susceptibility of an interacting electron gas of uniform density beyond the RPA. This RPA-beyond calculation suggests that with the more accurate diamagnetic susceptibility we may improve the performance of current-density functionals, especially when the density is away from the high-density regime. I plan to investigate spin-polarization effects by performing the calculations for spin-polarized densities. As an interesting test, I will apply the C-GGA and C-MGGA functionals developed in Refs. [23, 29] to first transition-metal atoms to investigate a class of complicated degeneracy problems.

3.3 van der Waals interaction correction

Exploration of the potential applicability of density functional approximations to van der Waals (vdW) systems is of considerable interest [50, 51]. Many physical properties and chemical and biochemical processes involve vdW interaction, such as physisorption, vdW complexes, and vdW bonds in crystals, liquids, adhesion, and soft condensed matter (e.g., biomacromolecules, biosurfaces, polymers, and membranes) [52, 53]. For example, vdW interaction is responsible for the heats of sublimation of hydrocarbon molecules and is significant for crystal packing of organic molecules, for orientation of molecules on surfaces, for the stacking of nucleic acids in DNA, and for solvent properties of polar and apolar compounds.

It has been shown that GGA density functionals can properly describe some dimers from this class of systems [30, 54, 55], as can hybrid functionals [55]. Recent test on rare-gas dimers shows [18] that the TPSS meta-GGA and the hybrid version describe the short-range part of vdW interaction well, while they are not adequate to describe the long-range part. This long-range interaction problem arises from the rapid exponential decay of the meta-GGA interaction. The performance of the meta-GGA functional may be improved by adding to it the long-range part of vdW interaction.

Recently I have constructed a model density functional to simulate the vdW coefficient C_6 and then have properly built it into the meta-GGA to construct a vdW-corrected meta-GGA functional. Application to rare-gas dimers shows that the vdW-corrected density functional yields fairly good bond lengths and binding energies. Encouraged by the result, I will apply this functional to other vdW systems such as benzene dimers, etc.

Alternately, since vdW interaction arises from correlation part of electron-electron interaction, it may be taken into account by a nonlocal functional [56]. This type of vdW density functionals could be accurate, but they are computationally demanding. Therefore, the long-range vdW interaction corrected density functional may be the first choice for the study of large molecular systems and solids.

3.4 Time-dependent dynamical potential

The development of the static DFT has reached a high level of sophistication. By contrast, the development of TDDFT is rather slow. Recently, we have presented a time- or frequency-dependent XC potential beyond the local density approximation. In this new scheme, the density gradient and other inhomogeneity parameter dependence of the nonadiabatic correction is introduced for the first time by applying the widely-used GGA and meta-GGA to the calculation of the XC stress tensor. The time- or frequency-dependent GGA and meta-GGA should allow a more accurate treatment of moder-

ately or strongly inhomogeneous systems exposed to low frequency fields, as, for example, in molecular transport problems, while remaining essentially exact for slowly varying densities and slowly varying time-dependent fields. However, in some cases such as in the double quantum well, the deformation of the ground-state density can be large, although it may be slowly varying in space. Furthermore, Our nonadiabatic correction depends upon two quantities: the bulk modulus and the shear modulus which can be obtained by an interpolation between the low- and high-frequency limits of them. While the low-frequency limit of the bulk modulus may be accurately calculated from the GGA and meta-GGA, an accurate estimate of the low-frequency limit of the shear modulus is still not available even for a system of uniform density. The best data available in the literature were obtained within the RPA [57] or via Landau parameters [58]. It has been found that the shear modulus (without s -dependence) plays an important role [59] in the description of the dynamical properties of long polymer chains.

First I plan to generalize our theory from the small deformation to the large one, but still retain the constraint of spatially slow variation of the deformation. Then I will calculate the low-frequency limit of the shear modulus beyond the RPA. Next I will construct a self-interaction-free dynamical potential, which is valid in the high-frequency regime, from the knowledge of the static DFT making use of a nonlinear coordinate transformation described in Ref. [47]. Self-interaction-free XC potentials are useful in many situations where self-interaction error is noticeable. Finally I will study the properties of our dynamical potentials when applied to real systems. As an interesting example, I will use them to calculate the excitation energies of atoms [60].

3.5 Continuum mechanics for nanoscale systems

While working on the development of TDDFT, I have come to realize that there is a distinct possibility of formulating the excitation energy of nanoscale systems as a continuum mechanics problem. For example, the exact equation of motion for the current in a molecule leads to an eigenvalue problem from which one can obtain in principle all the excitation energies and the corresponding eigenfunctions (which are just matrix elements of the current operators between eigenstates of the Hamiltonian). I plan to deepen my understanding of this promising formulation, which appears to be closely related to the memory-function formalism and to propagator methods in quantum chemistry. A major challenge will be the construction of the stress tensor (which appears in the equation of motion for the current) as a functional of the current. I hope that a better understanding of the analytic structure of the stress tensor as a function of frequency will enable me to express this key quantity in terms of linear response functions that can be calculated in terms of Kohn-Sham spectral distributions. Then perhaps the power of the numerical techniques recently developed by the Trieste group [61] for evaluating Kohn Sham spectra can be brought to bear on this fundamental problem of many-body theory.

Because the stress tensor of one-electron systems is known exactly, as a first effort toward this new idea, I have studied the continuum mechanics for one-electron systems. Calculation shows that the continuum mechanics within the linear response is exact for one-electron systems: It exactly yields all the excitation spectra and transition currents. We can show that the theory can be made exact in the high-frequency limit. So next I will turn to the continuum mechanics for many-electron systems. Calculation of excitation energies of molecules is of general interest and significantly importance in chemistry.

3.6 Stress tensor in magnetic fields

I have recently calculated with my collaborators the stress tensor from DFT and then constructed a physically-motivated electron localization function (ELF) from the trace of the stress tensor—the electronic pressure [35]. Application to atoms shows that the new ELF reveals all the atomic shell structure very well.

Since the pressure is a physical quantity and should be gauge invariant. Furthermore, it should remain the same for electrons occupying different degenerate states. However, the pressure we have calculated depends upon the Kohn-Sham kinetic energy, which is gauge-dependent, the new ELF fails to reproduce the correct degeneracy for open-shell atoms and molecules. To fix this problem, what we need to do is to reformulate the stress tensor in magnetic fields. First I will calculate the stress tensor in magnetic fields. Then I will apply it to the calculation of the pressure for open-shell atoms and molecules. Finally I will also extend our formulation to the time-dependent or excited states to study how and where electrons are localized.

3.7 Static and time-dependent DFT for low-dimensional systems

Electrons localized at the surface of metals can provide a natural realization of two-dimensional systems [38]. The electronic states at the surface have an exponential decay along the direction perpendicular to the surface, while they are fully delocalized in the plane of the surface. This has been vividly visualized by means of low temperature scanning tunneling microscopy techniques [62]. The development of semiconductor electronics has made a major impact on the study of low-dimensional systems. It is now possible to fabricate high-quality Si- and GaAs-based quantum wells *a* in which the carriers motion is quantized. By making the quantum well width appropriately small (i.e., $na \ll 1$), we can create a situation in which the energy separation between the two lowest subbands is much larger than the characteristic kinetic energy of the in-plane motion. As long as there is not enough energy to populate higher subbands, we can effectively realize a two-dimensional electron gas. In this situation, all the electrons reside in the lowest subband and their kinetic energies depend on just the two-dimensional wave vector (in the x-y plane).

The most interesting feature of 2D systems is that there is a possibility of studying the electron-electron interaction in a variety of density regimes by varying the electron density over an unprecedentedly broad range. Control over the density can be achieved by electrical means, i.e., by changing the voltage of certain control electrodes (known as gates). An important technological application of 2D systems is the replacement of the time-honored bipolar transistor of Bardeen, Brattain, and Shockley with an MOS-based field-effect transistor (MOSFET) in contemporary computer chips.

Experimental studies of quasi-one-dimensional conductors began with the discovery of the first organic conductor, the charge-transfer salt TTF-TCQN (tetrathiafulvalene-tetracyanoquinodimethane). This is a highly anisotropic material comprised of chains of molecules with a large room temperature conductivity along the chain direction. The material stays metallic down to a temperature of 53 K where it undergoes a charge-density-wave transition to an insulating state. Although the systems are anisotropic, they do not satisfy the technical condition for quasi-one dimensionality that all the electrons should reside in a single one-dimensional subband.

Examples of true one-dimensional systems are provided by etching nanowires on the surface of semiconductors, as demonstrated in a landmark experiment [63] which proved the quantization of conductance of clean quantum wires in integer multiples of e^2/h . A very promising class of quasi-1D systems are carbon nanotubes [64]. In contrast to organic polymers these systems have a relatively simple, one-dimensional band structure [65] and thus can be used as model systems for studies of many-body effects

in low-dimensional systems.

The development of density functional theory is fast for 3-dimensional (3D) systems. In particular, the static DFT has reached a high level of sophistication for 3D systems. Although the study of many-body effects for low-dimensional systems is significantly important in developing molecular electronic devices, the development of the DFT methods for those systems is rather slow. So far the only approximation available in the literature is the local density approximation (LDA) [66]. As a long-term plan, I will develop the static and time-dependent density functional theory for low-dimensional inhomogeneous systems.

3.8 Ultrafast optical phenomena in strongly correlated electron materials

Ultrafast optical spectroscopy is significantly important for the study of the dynamical properties of molecules and solids at the fundamental timescales of nuclear and electronic motion. Due to the dramatic improvement of short-time pulse experimental techniques many important advances in femtosecond optics have been achieved in recent years. It has been used to investigate the dynamics of metals and semiconductors. Its application to strongly correlated electron systems is in the pioneering stage.

Since in many femtosecond experiments, the dynamics can be interpreted from the knowledge of changes in the complex dielectric function ϵ , accurate calculation of this quantity is a key for the understanding of experimental results. Theoretically, two popular approaches can be used to describe electronic excitations: Bethe-Salpeter many-body approach and TDDFT. At the femtosecond timescale, Bethe-Salpeter approach becomes very complicated. The method of choice is TDDFT.

I plan to employ a TDDFT method with the dynamical XC potentials beyond the adiabatic LDA (ALDA) to calculate the dielectric function. Specifically, I will explore the possibility of building the meta-GGA into the time-dependent current-density functional theory, where a nonadiabatic correction for the slowly-varying external potential is used. The goal of this study is to provide a theoretical foundation for ultrafast optical spectroscopy experiments on strongly correlated electron materials. To fulfill this goal, I plan to take the following path: First I am going to apply this new approach to large molecules (e.g., carbon nanotubes) to see whether the Rydberg series, which is missing in the TDDFT-ALDA calculations, can be restored. Secondly, I will also apply this technique to simple semiconductors to see to what extent the ALDA absorption spectra can be improved. These two steps will help me improve the new approach. Given the complexity inherent in the application to the real materials, I will also perform the model analysis to gain a deeper understanding of various issues.

3.9 Application of DFT/TDDFT to nanoscale systems

Development of high-performance organic light-emitting diodes (OLEDs) [67] plays a crucial role in the fabrication of high-resolution, full-color, and flat-panel displays [68]. The advantage of the OLEDs over the conventional inorganic semiconductor materials such as silicon and germanium is ultralow cost, light weight, and flexibility. Furthermore, because of the ability to deposit organic films on any low-cost substrates [68, 69] such as glass, plastic, or metal foils, OLED materials are particularly well suited for large-area displays [70]. Successful commercial production of organic electrophotographic imaging [71] for copiers, printers, and projection TV benefits from the improvement of material properties and optimization of device structure for OLEDs to enhance brightness, power efficiency, luminescence efficiency, and color purity of the three primary electroluminescence (EL) colors (red, green, and blue).

In recent years, a series of experimental measurements of the dynamical properties of light-emitting materials have been performed. However, theoretical investigation of dynamical properties based on *ab*

initio methods have been limited. Such theoretical investigation can lead to a better understanding of molecular electronic excited states, which is significantly important in the study of spectroscopy and photochemistry. In particular, it provides a relevant guide for the design and improvement of optical materials.

I will apply DFT/TDDFT to such optical materials to study their static and dynamical properties such as ionization potential, electron affinity, excitation energy, and absorption spectrum.

This proposal involves the education of both undergraduate and graduate students. The expanded version should be suitable to apply for external funds. Students may contribute ideas on new methods or perform numerical studies or do both.

Start-up requirements: Approximately \$75,000 for Computers, codes, etc.

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